

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A251 176



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2. REPORT DATE

5/26/92

3. REPORT TYPE AND DATES COVERED

Technical - 1 June, 1991 - 31 May, 1992

4. TITLE AND SUBTITLE

Formation of Compound Semiconductors by
Electrochemical Atomic Layer Epitaxy (ECALE)

5. FUNDING NUMBERS

G-N00014-19-J-1919

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University of Georgia
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REPORT NUMBER

Technical Report #5

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Chemistry Division
Arlington, VA 22217-500010. SPONSORING / MONITORING
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

DTIC
ELECTE
S B D
JUN 09 1992

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release and sale; its distribution
is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A method for the electrochemical formation of epitaxial deposits of compound semiconductors is being developed. It is referred to as Electrochemical Atomic Layer Epitaxy (ECALE). The method is the electrochemical analog of Atomic Layer Epitaxy (ALE), where ALE is a method used to form compounds by alternately depositing atomic layers of the constituent elements. Atomic layers are formed in ECALE by using Underpotential Deposition (UPD). UPD is a phenomena where an atomic layer of an element deposits at a potential prior to that needed to deposit the bulk element, due to the increased stability afforded by reaction with a second element present at the substrate surface. This paper describes the structure of the first monolayer of Te formed on a Au(100) surface and the structure of a monolayer of CdTe, subsequently formed by deposition of an atomic layer of Cd. Deposits have been formed and analyzed in a UHV surface analysis instrument directly coupled to an electrochemical cell. LEED and Auger electron spectroscopy have been used to follow the structures and compositions of deposits after various steps in the ECALE cycle. As well, some initial studies of the atomic arrangements have been performed using scanning tunneling microscopy.

14. SUBJECT TERMS

Epitaxy, ALE, Electrodeposition, CdTe, Gold Single Crystals

15. NUMBER OF PAGES

33

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

Unclassified

18. SECURITY CLASSIFICATION
OF THIS PAGE

Unclassified

19. SECURITY CLASSIFICATION
OF ABSTRACT

Unclassified

20. LIMITATION OF ABSTRACT

UL

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-91-J-1919

R&T Code 4133036

Technical Report No. 5

**Formation of Compound Semiconductors by
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by

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Brian W. Gregory and John L. Stickney**

Prepared for Publication

in the

Journal of Vacuum Science and Technology A

**University of Georgia
Department of Chemistry
Athens, GA**

May 26, 1992

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92 6 05 015

92-14888


FORMATION OF COMPOUND SEMICONDUCTORS BY ELECTROCHEMICAL ATOMIC
LAYER EPITAXY (ECALE)

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ABSTRACT

A method for the electrochemical formation of epitaxial deposits of compound semiconductors is being developed. It is referred to as Electrochemical Atomic Layer Epitaxy (ECALE). The method is the electrochemical analog of Atomic Layer Epitaxy (ALE), where ALE is a method used to form compounds by alternately depositing atomic layers of the constituent elements. Atomic layers are formed in ECALE by using Underpotential Deposition (UPD). UPD is a phenomena where an atomic layer of an element deposits at a potential prior to that needed to deposit the bulk element, due to the increased stability afforded by reaction with a second element present at the substrate surface. This paper describes the structure of the first monolayer of Te formed on a Au(100) surface and the structure of a monolayer of CdTe, subsequently formed by deposition of an atomic layer of Cd. Deposits have been formed and analyzed in a UHV surface analysis instrument directly coupled to an electrochemical cell. LEED and Auger electron spectroscopy have been used to follow the structures and compositions of deposits after various steps in the ECALE cycle. As well, some initial studies of the atomic arrangements have been performed using scanning tunneling microscopy. Reductive UPD of Te on the Au(100) plane resulted in a series of well ordered Te structures at increasing coverages: (2X2), (2X $\sqrt{3}$ 7), (2X4) and ($\sqrt{2}$ X $\sqrt{5}$)R45°. Oxidative UPD of Te also resulted in a well ordered structure, a (2X $\sqrt{10}$) at 1/3 coverage of Te. Subsequent reductive UPD of Cd on this surface resulted in a well ordered c(2X2)-CdTe

structure.

INTRODUCTION

Electrodeposition is being investigated as a low cost, flexible, low temperature method for the formation of compound semiconductors [1-3]. Encouraging results have been obtained by a number of workers [4-10]. Difficulties encountered involve the ubiquitous formation of polycrystalline deposits. This group is presently developing methods for controlling deposit structure, with the aim of epitaxially electrodepositing compound semiconductors.

Central issues in the epitaxial electrodeposition of compound semiconductors are substrate structure and control over nucleation and growth. Previous studies of the electrodeposition of compound semiconductors have been performed exclusively on polycrystalline substrates [4-10]. In the present research, well-characterized single-crystal substrates are used to investigate the electrodeposition of compound semiconductors. Further, in currently practiced methods of compound semiconductor electrodeposition, control over nucleation and growth processes is essentially absent [6]. The electrode potential is adjusted to optimize stoichiometry and cannot be used to control nucleation.

The method of electrochemical atomic layer epitaxy (ECALE) is currently being developed in our group in order to gain control over three-dimensional growth in the electrodeposition of compound semiconductors [12,13]. The method involves the alternated

electrodeposition of atomic layers of the constituent elements which make up a compound. Deposition is limited to an atomic layer by the use of underpotential deposition (UPD) [14,15]. UPD refers to a surface-limited process whereby a depositing element forms a compound with substrate surface atoms. Deposition of the element proceeds until the surface is "covered".

ECALE is the electrochemical analog of Atomic Layer Epitaxy (ALE) [16-19]. ALE refers to a series of techniques where a compound is formed a monolayer at a time by the alternated deposition of atomic layers of the constituent elements. ALE is applicable to a variety of thin film formation methods such as Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD), Metal Organic chemical Vapor Deposition (MOCVD) etc.. In the formation of a compound such as GaAs by ALE in the MOCVD mode, a flux of H_3As , an arsenic precursor gas, is exposed to the substrate surface at a temperature which allows formation of a single As surface layer. All excess H_3As is subsequently pumped away. The As atomic layer is stabilized by compound formation with previously deposited Ga. A flux of tetramethyl gallium (TMG), a gallium precursor gas, is then exposed to the surface, and similarly an atomic layer of Ga is formed. Excess gas is pumped away. Thin films are produced by repeating this cycle [20-23]. It is from ALE that the concept of ECALE was developed.

Use of UPD in order to electrodeposit atomic layers of both elements, at present, requires that one element be deposited by reductive UPD while the other is deposited by oxidative UPD [13].

In this way, one underpotentially deposited element can be held on the surface at the potential used subsequently to deposit the other element. In the formation of a compound such as CdTe, Te can be oxidatively underpotentially deposited from Te^{2-} at a fairly negative potential. Cadmium can next be reductively underpotentially deposited from a Cd^{2+} solution at a more positive potential, where the previously deposited Te remains stable.

UPD potential shifts are an indication of the free energy of formation of a compound from the solution species and are chosen prior to (under) those necessary for deposition of the bulk elements. Figure 1 graphically describes UPD of Cd and Te in the formation of CdTe using potential vs. pH, Pourbaix, diagrams [24]. Figures 1A and 1B are the Pourbaix diagrams for Cd and Te respectively, calculated for an activity of 10^{-3} M for all soluble species, in water. Figure 1C is an equivalent Pourbaix diagram for formation of the compound CdTe by reduction of Cd^{+2} and oxidation of Te^{2-} . Figure 1D is the superposition of the first three diagrams to point out the significantly increased stability of the deposited Te and Cd, resulting from deposition on CdTe as opposed to the pure elements. Stabilization energies of over 400 mV are calculated at all pH values for both the reductive deposition of Cd and the oxidative deposition of Te. For a given deposition, variations will necessarily be encountered due to surface structure effects and changes in the activity of the surface as the deposition proceeds. In other words, the activities of the bulk species, including CdTe, were assumed to be unity. It

is clear that as a surface excess of one element is converted to a surface excess of the second element during deposition, very significant changes in the activity of the CdTe surface should have been incorporated into the calculations.

Currently, ECALE appears most applicable to the formation of compound semiconductors which include at least one of the following elements: Tellurium, Selenium, Sulfur, Arsenic, or Antimony. These are elements which may be obtained as soluble species in a negative oxidation state (e.g., telluride ion), thus facilitating oxidative UPD. The second element, in a compound semiconductor to be formed by ECALE, is less restrictive as it is deposited by reductive UPD from a precursor species where it is present in a positive oxidation state.

Initial work on ECALE has centered on the deposition of CdTe [11-13]. Previous studies include investigations of the potentials and coverages for Cd and Te UPD on polycrystalline Pt, Cu and Au electrodes in thin-layer electrochemical cells (TLEs) [11]. That study was performed to determine the best substrate to use in investigations of CdTe deposition by the ECALE method. A second article described the first ECALE deposition, where two monolayers of CdTe were formed on a polycrystalline Au TLE [12].

The conditions for the ECALE deposition of CdTe on Au electrodes were discussed in a subsequent article [25]. The work presented here is a continuation of studies of ECALE on well-defined single-crystal electrodes. Previously, studies were performed to investigate the structures resulting from UPD of Te on the low-

index planes of Au [26]. Initial studies into the preparation of CdTe single crystals surfaces in solution [27] have been performed as well, in anticipation of subsequent studies of homoepitaxy. Besides work on the deposition of CdTe, initial investigations into the deposition of GaAs by ECALE have also been undertaken [28,29].

The present studies have been performed on Au electrodes as Au is an excellent electrode material. It has a large potential window over which no faradaic reactivity is observed in aqueous electrolyte solutions. This is advantageous for studies of the deposition of other elements. Lattice matching was not a consideration in the choice of Au as the substrate material.

EXPERIMENTAL

The instrumentation and procedures used in these studies have been described in a previous article [30]. Two Au single crystals were used in the present studies: a "tri"-crystal which had three main faces, each oriented to a different low-index plane; and a (100) "six-sided" crystal, where each face was polished to the (100) or an equivalent plane. The tri-crystal was used so that deposition occurred on the three faces under equivalent conditions. The six-sided crystal was used such that the observed electrochemical reactivity would correspond to a single atomic geometry. The six-sided crystal, as opposed to crystals oriented and polished on a single side, has a more defined geometric surface area, which is helpful in coulometric measurements. Studies involving LEED and Auger electron spectroscopy were performed using

the tri-crystal in a UHV surface-analysis instrument coupled to an antechamber containing an electrochemical cell. In this way, deposit surfaces were investigated without exposure to air. Sample preparation procedures involved both ion bombardment and annealing, followed by LEED and Auger spectroscopic analysis of the surfaces. These procedures were performed prior to each experiment in order to ensure that the surfaces were clean and ordered.

Auger spectra were recorded with an off-axis electron gun (45°) and a hemispherical electron energy analyzer (Leybold Heraeus). Beam currents were kept below $5.0 \mu\text{A}$, with a spot size of 0.5 mm^2 . Scans were run from 100-600 eV. Scan times were 5 minutes. Sequential scans indicated no detectable beam damage from the above conditions.

Scanning tunneling microscopic (STM) investigations were performed at atmospheric pressure in a nitrogen filled glove box with a Nanoscope II from Digital Instruments. Sample preparation involved flame annealing followed by potential cycling, inside the glove box, in sulfuric acid. A representative voltammogram for the clean six-sided Au(100) crystal is displayed in Figure 2a [31]. Solutions used were made from pyrolytically, triply-distilled water [32]. The sulfuric acid was made with Johnson Matthey fuming sulfuric acid, due to the lower levels of residual chloride found in these solutions compared with those made with Baker Analyzed reagent grade sulfuric acid [33]. Tellurium was obtained from Johnson Matthey as TeO_2 (99.9995%) and dissolved as such in concentrated sulfuric acid, prior to dilution and adjustment to the

final pH. Ultrapure anhydrous cadmium sulfate was obtained from Alfa products.

Electrochemical experiments were performed in an all-Pyrex cell using a standard three-electrode potentiostat. The auxiliary electrode consisted of a Au wire and the reference electrode was Ag/AgCl made with 10 mM NaCl, or Ag/Ag₂CrO₄ (10 mM K₂CrO₄) in order to minimize chloride contamination. All potentials are reported with respect to a Ag/AgCl reference electrode prepared with 1.0 M NaCl.

Results and Discussion

The following studies were performed to investigate the structures formed during the initial stages of CdTe deposition on Au by ECALE. Either Cd or Te can be used to form the initial atomic layer of CdTe on Au. For the investigations described here, Te was deposited first since it showed greater stability in an aqueous environment. When Cd was the first element deposited, subsequent "emersion" (withdrawal from solution) resulted in the spontaneous formation of cadmium oxides or hydroxides on the surface. This is a natural consequence of the instability of elemental Cd in the presence of water [24]; elemental Cd is only stable while the substrate is under potential control. The procedure used to study surface structures in the present investigations involved loss of potential control during emersion, leading to the spontaneous reaction of Cd and water. Significant amounts of oxygen were present in the resulting Auger spectra, and diffuse LEED patterns were evident on the surface after emersion.

Loss of potential control can be avoided by use of an electrochemical flow cell where solutions are changed without emersion. Cells of this nature are presently being used in our group to form thicker deposits in an automated electrodeposition system.

Te deposition on Au(100) from a TeO_2 solution is shown in Figure 2b. Evident in the reduction are three distinct regions: two underpotential regions followed by bulk Te deposition. A plot of Te coverage as a function of potential, and the LEED patterns

observed after emersion at selected potentials, are displayed in Figure 3 for the (100) plane of Au. Evident in Figure 3 are changes in the observed LEED patterns accompanying the changes in coverage associated with the reduction features in Figure 2b. Preliminary results from STM are displayed in Figure 4 for two Te structures: a $1/4$ coverage (2×2) structure and a $1/3$ coverage ($2 \times \sqrt{3}$) structure.

Proposed structures consistent with the data listed above are depicted in Figure 5. Initial deposition through the first UPD peak results in a $1/4$ coverage of Te. A simple (2×2) structure with isolated Te atoms is consistent with the LEED pattern and the observed coverage. The micrograph shown in Figure 4a depicts a (2×2) arrangement of Te atoms at $1/4$ coverage, but with a significant amount of phase shifting, where adsorbate atoms appear to shift from one four-fold site in the (2×2) unit cell to another. Close inspection reveals the presence of some dimerization on the surface, generally associated with the zones where phase shifting has occurred. Other areas on the same Te covered Au(100) face, evidence domains of dimers, at a higher Te packing density. The formation of dimers was not unexpected and had been predicted in a previous paper [26]. Similar dimer structures have been observed in other studies, such as arsenic deposition on Au(100) performed in this laboratory. As well, trimer, tetramer and hexamer structures have previously been observed with STM for the chalcogen S on Re(111) [34].

Corresponding LEED patterns for deposition through the first

UPD peak indicated only the presence of a (2X2) structure on the surface. In fact, unit cells consistent with higher coverage dimer structures were not observed with LEED until the potential was shifted another 200mV further negative. Presently it appears that the (2X2) resulted from the deposition of isolated Te atoms, loosely packed at a distance of 0.58 nm, which is significantly greater than Te's van der Waal's diameter (0.44 nm) [35].

Just as reductive UPD of TeO_2 results in atomic layers of Te (Figure 2b), an atomic layer of Te is also formed by oxidative UPD from a reduced Te species such as Te^{2-} . Alternatively, bulk Te can be reductively dissolved, forming Te^{2-} for example, leaving an atomic layer of Te. Aqueous Te^{2-} solutions made from salts such as Na_2Te are very unstable and hard to work with. For that reason studies of oxidative UPD were performed as stripping experiments, where atomic layers of Te were formed by reduction of TeO_2 to form bulk Te and then reduced at -1.3 V for 30 seconds in a borate buffered solution containing no Te species to convert the bulk Te to Te^{2-} . The result, on Au(100), was formation of a (2X√10) LEED pattern at a Te coverage of 1/3.

A STM micrograph depicting the structure responsible for the (2X√10) pattern is shown in Figure 4b. One interpretation of the micrograph suggests the presence of dimers or, alternatively, zig-zag chains of Te atoms. The distances appear to be close to the √2 distance for the Au(100) surface (0.42 nm). The positioning of the Te atoms with respect to the Au substrate is not clear from the

micrographs but previous studies of chalcogenides on metals suggest high-coordinate sites [36].

A structure proposed to account for the observed (2×10) pattern is displayed in Figure 5b. The structure can be interpreted as dimers or chains, where all atoms are located in, or close to, four-fold sites. This Te-Te distance, 0.42 nm, is slightly less than the van der Waal's diameter for Te. From the micrograph it appears that the atoms are not in identical sites, every other atom appears to sit higher. This may indicate that $1/2$ the atoms are in optimal 4-fold sites while the remaining are slightly out of position, resulting in the atoms which sit higher on the surface.

Coverages from Auger, and LEED patterns observed, for the deposition of Cd on the Au(100) (2×10) -Te surface are depicted in Figure 6. A (2×10) LEED pattern was still evident at deposition potentials above -0.3V, although diffuse intensity has increased. Below -0.3V a new pattern was observed: a $c(2\times 2)$. This pattern persisted over a range of about 100 mV, at which point the pattern became completely diffuse. It appears that the optimal stoichiometry for the structure responsible for the $c(2\times 2)$ LEED pattern is 1:1, as might be expected. At potentials below -0.4V bulk Cd is beginning to form, as can be seen by the steep increase in the Cd Auger signal. Also evident is the lack of an oxygen Auger signal at low Cd coverages, corresponding to the $c(2\times 2)$. Studies of Cd UPD directly on Au(100) resulted in significant oxygen

signals as mentioned previously. This lack of oxygen signal on the ECALE CdTe monolayer is consistent with the formation of stoichiometric CdTe, which has been shown to be essentially inert under equivalent conditions using a CdTe(111) single crystal [27]. The increase in oxygen with the decreasing deposition potential, below -0.4V, is also consistent with the formation of bulk Cd.

A proposed structure for the c(2X2) unit cell is shown in Figure 7. The small unit cell, containing only 2 substrate atoms, severely limits the number of possible structures. The only logical coverages for Cd and Te would be 1/2 for each. Alternatively, full coverage might be possible, but coverage measurements from both stripping coulometry and Auger indicate 1/2 coverage. Another question that can be raised is which element is on top? Presently, the answer is not clear, as equivalent experiments have been performed where Cd was deposited first followed by Te. The results were essentially the same: a c(2X2) LEED pattern at a 1:1 Cd to Te stoichiometry.

In the deposition of Cd on Au(100)(2X√10)-Te, the initial coverage of Te is 1/3 (Figure 5b). However, the coverage proposed for the c(2X2)-CdTe structure is 1/2 for both Cd and Te. Use of higher coverages of Te, such as the (2X4) structure (Figure 3) at 1/2 coverage, also resulted in the c(2X2)-CdTe structure with some increased clarity for the resulting LEED pattern. It appears that the c(2X2) is the most stable structure, and the extent of its formation is a function of the limiting reagent, not the structure of the initially deposited atomic layer nor the identity of the

initially deposited element. Reproducible formation of a surface supporting only the (2X4)-Te structure, at 1/2 coverage of Te, was, however, difficult as the potentials separating the formation of the (2X $\sqrt{3}$ 7), the (2X4), and the ($\sqrt{2}$ X $\sqrt{5}$) structures were relatively small (Figure 3). This led to the cohabitation of the surface by at least two of the above structures under most deposition conditions between 0.13 and 0.0 V [26].

Figures

Figure 1. Pourbaix diagrams describing A) Cd, B) Te, C) CdTe and D) the underpotential deposition of Cd and Te on CdTe, in water. The diagrams were calculated using an activity of 10^{-3} M for all soluble species. The hatched areas in D represent the differences in potentials, UPD, associated with deposition on CdTe as opposed to deposition on the pure elements.

Figure 2. Voltammetry for the six-sided Au(100) crystal. A) Voltammetry corresponding to a clean (100) surface in 10 mM H_2SO_4 . B) Voltammetry corresponding to Te deposition from a 0.25 mM TeO_2 , 20 mM H_2SO_4 solution.

Figure 3. A plot of the coverage of Te on the surface of a Au(100) crystal as a function of potential. Also displayed in the figure are the LEED patterns observed after emersion at various potentials, during the deposition.

Figure 4. STM micrographs of Te structures on Au(100). A) Au(100)(2×2)- $1/4$ coverage Te; B) Au(100)($2\times \sqrt{10}$)- $1/3$ coverage Te. Both micrographs are unfiltered.

Figure 5. Proposed structures for the deposition of Te on Au(100). A) Au(100)(2×2) at $1/4$ coverage; B) Au(100)($2\times \sqrt{10}$) at $1/3$ coverage of Te.

Figure 6. A plot of Cd coverage as a function of the Cd deposition potential on a Au(100)(2X√10)-Te structure. LEED patterns observed after emersion at the various potentials are also noted in the figure.

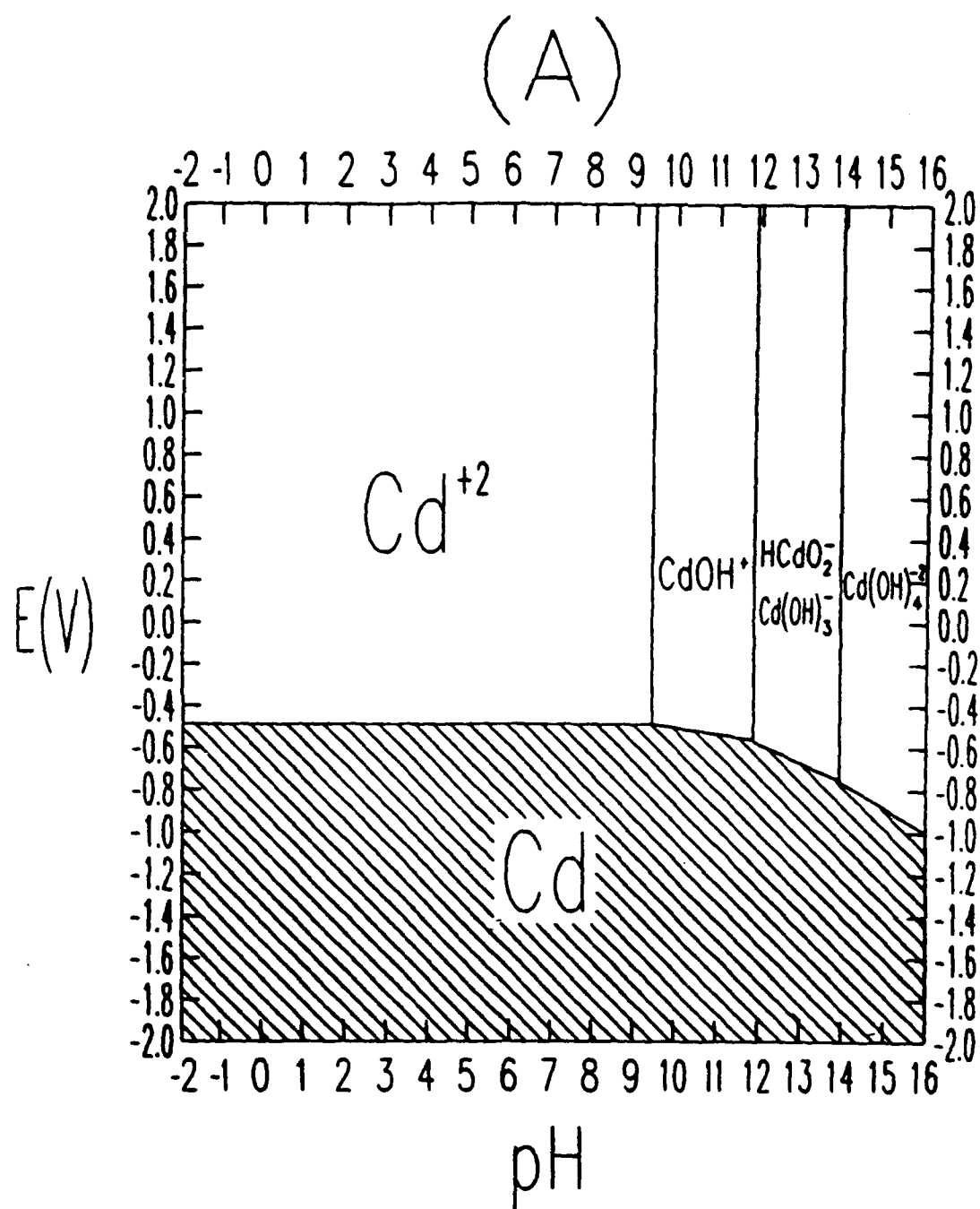
Figure 7. Proposed structure for the ECALE deposition of a monolayer of CdTe on Au(100).

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Figure 1a - Suggs, *et. al.*



(B)

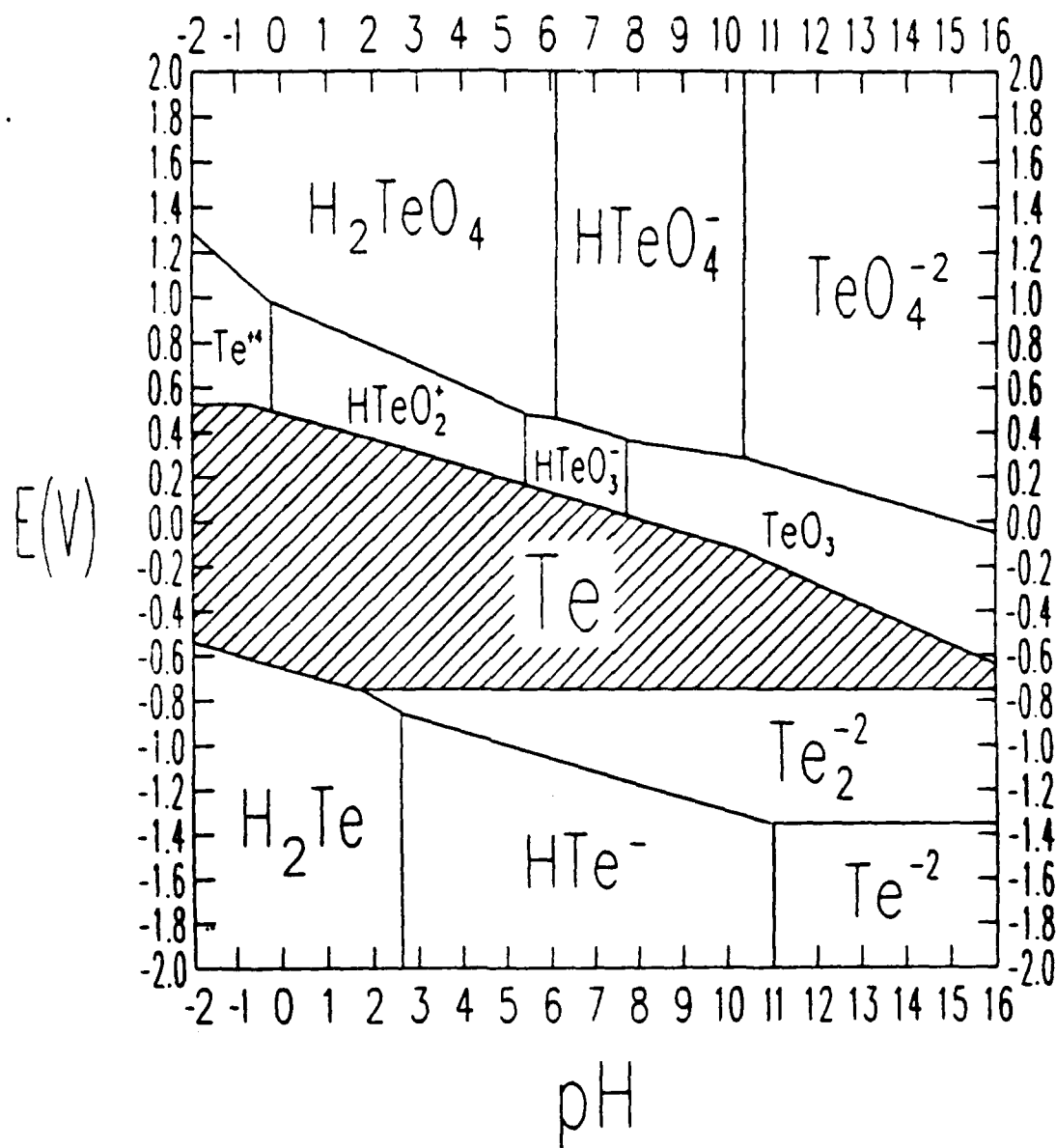


Figure 1c - Suggs, et. al.

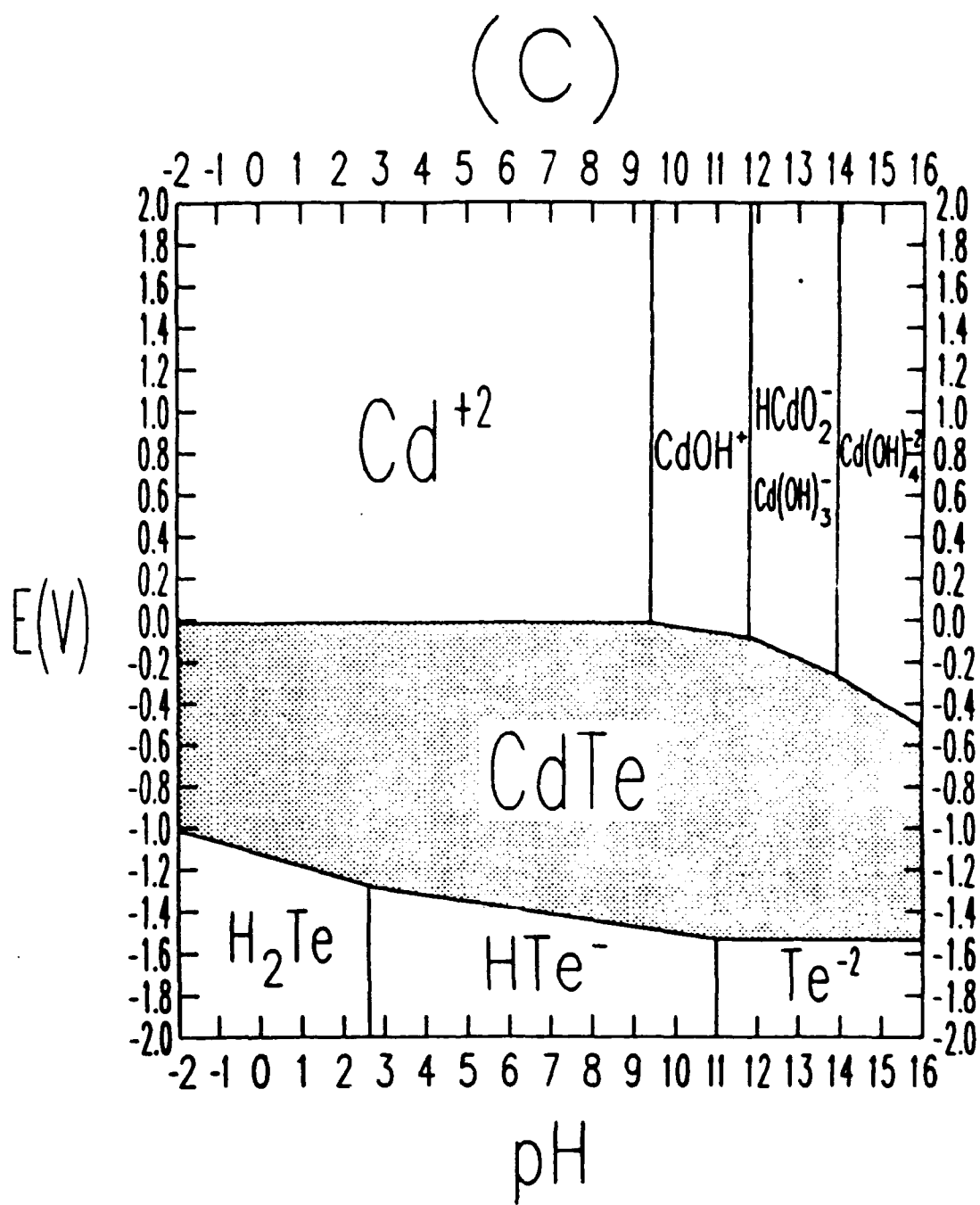


Figure 1d - Suggs, et. al.

(D)

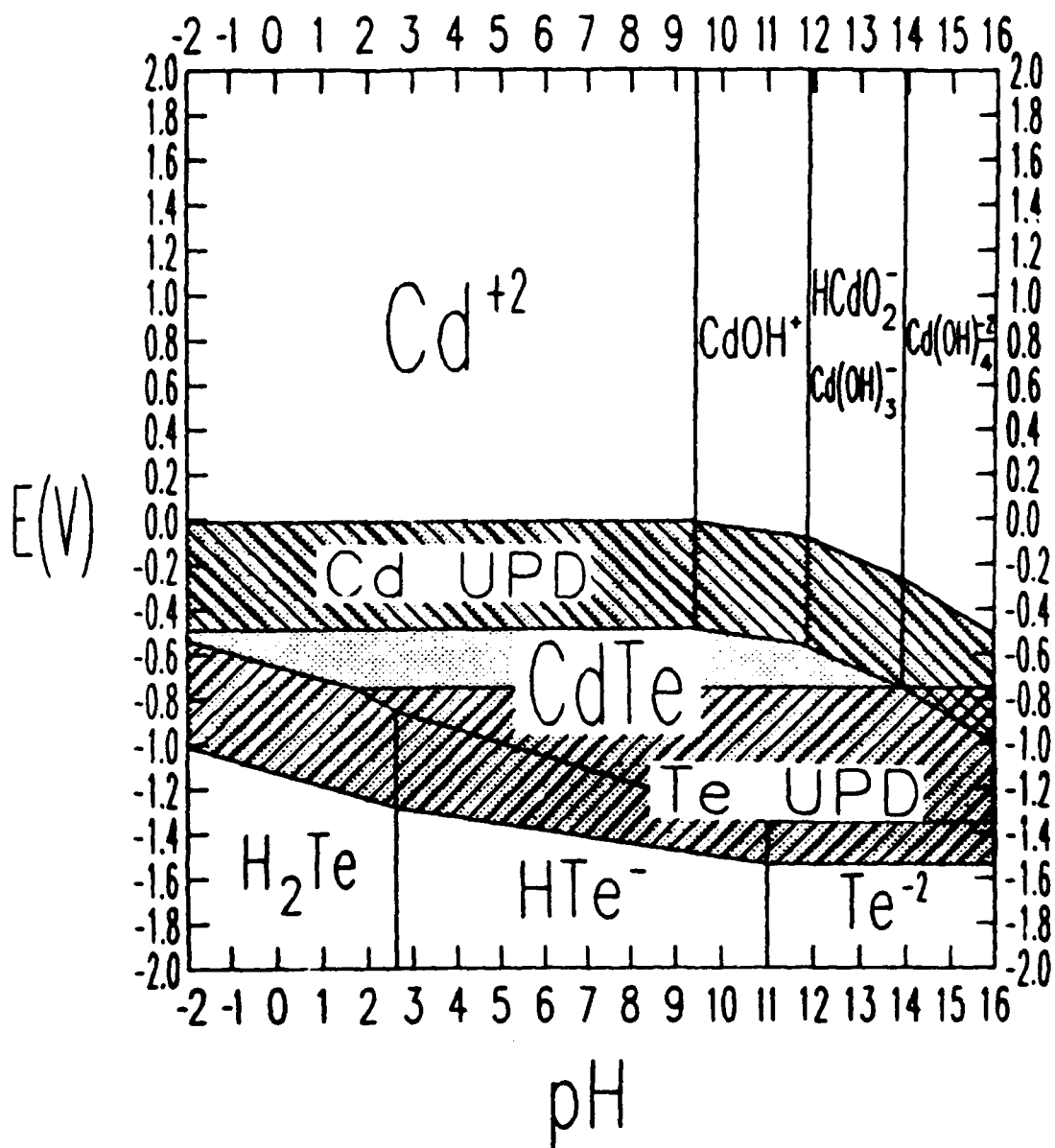


Figure 2 - Suggs, et. al.

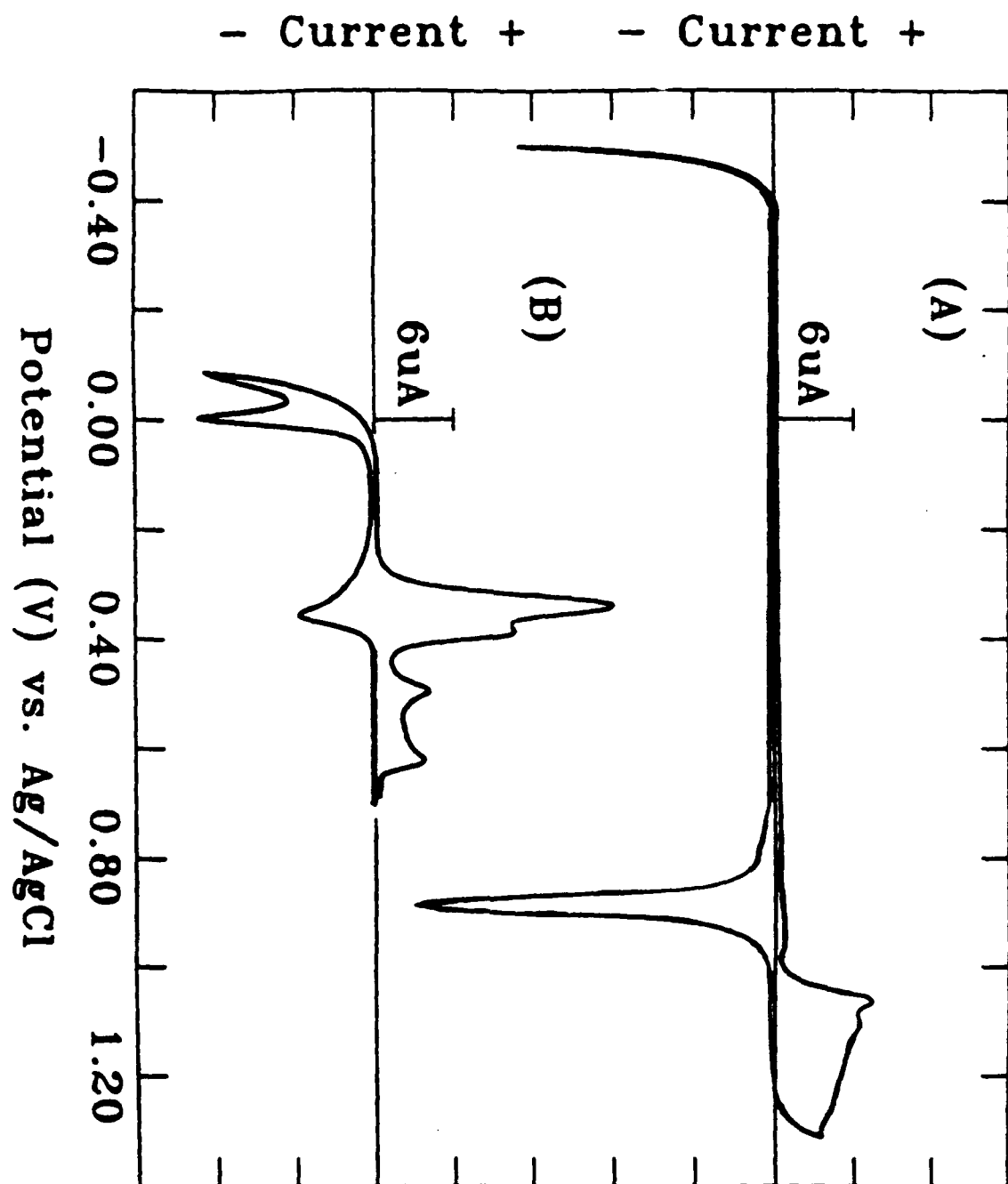


Figure 1, Suggs et al.

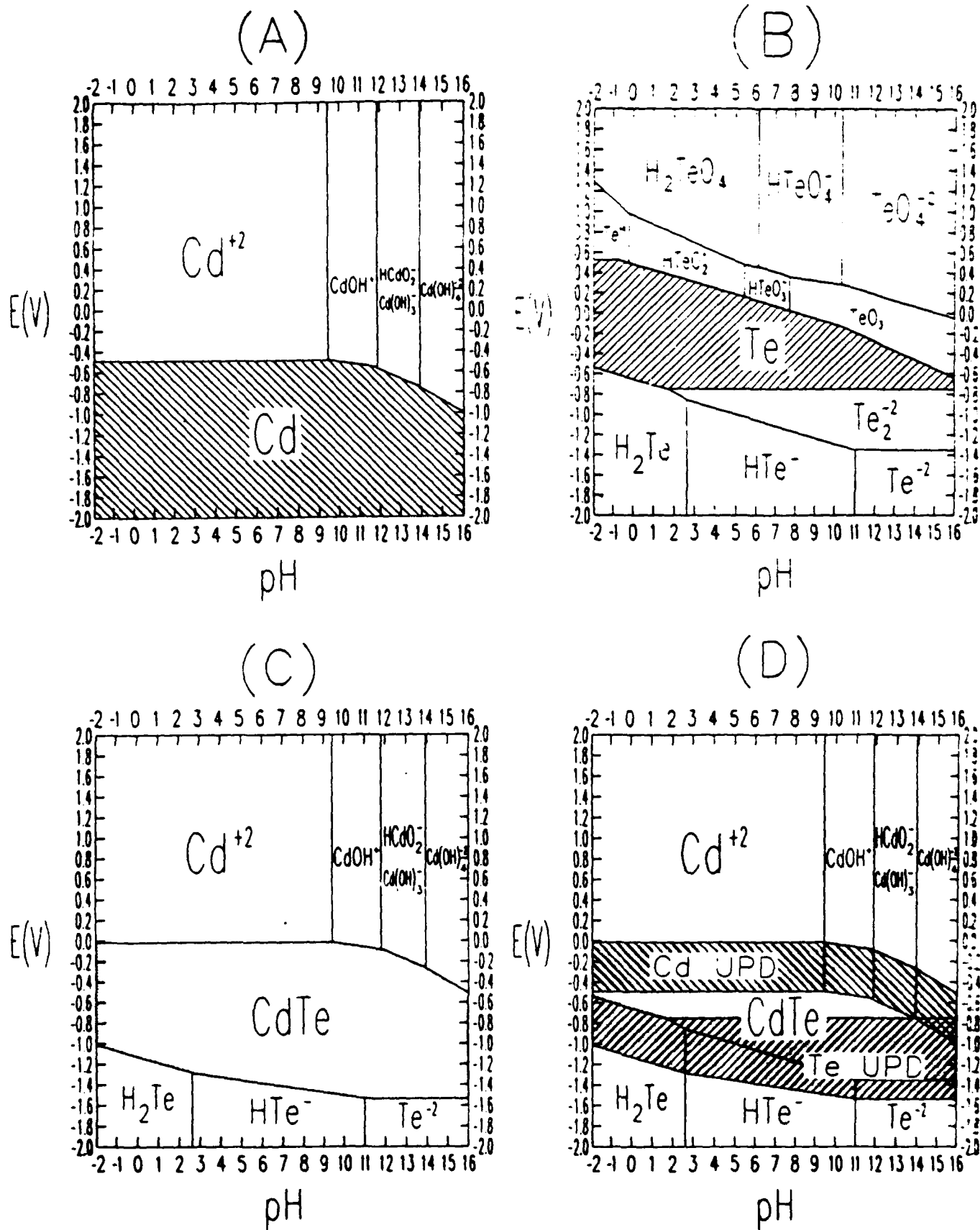


Figure 2 - Suggs, et. al.

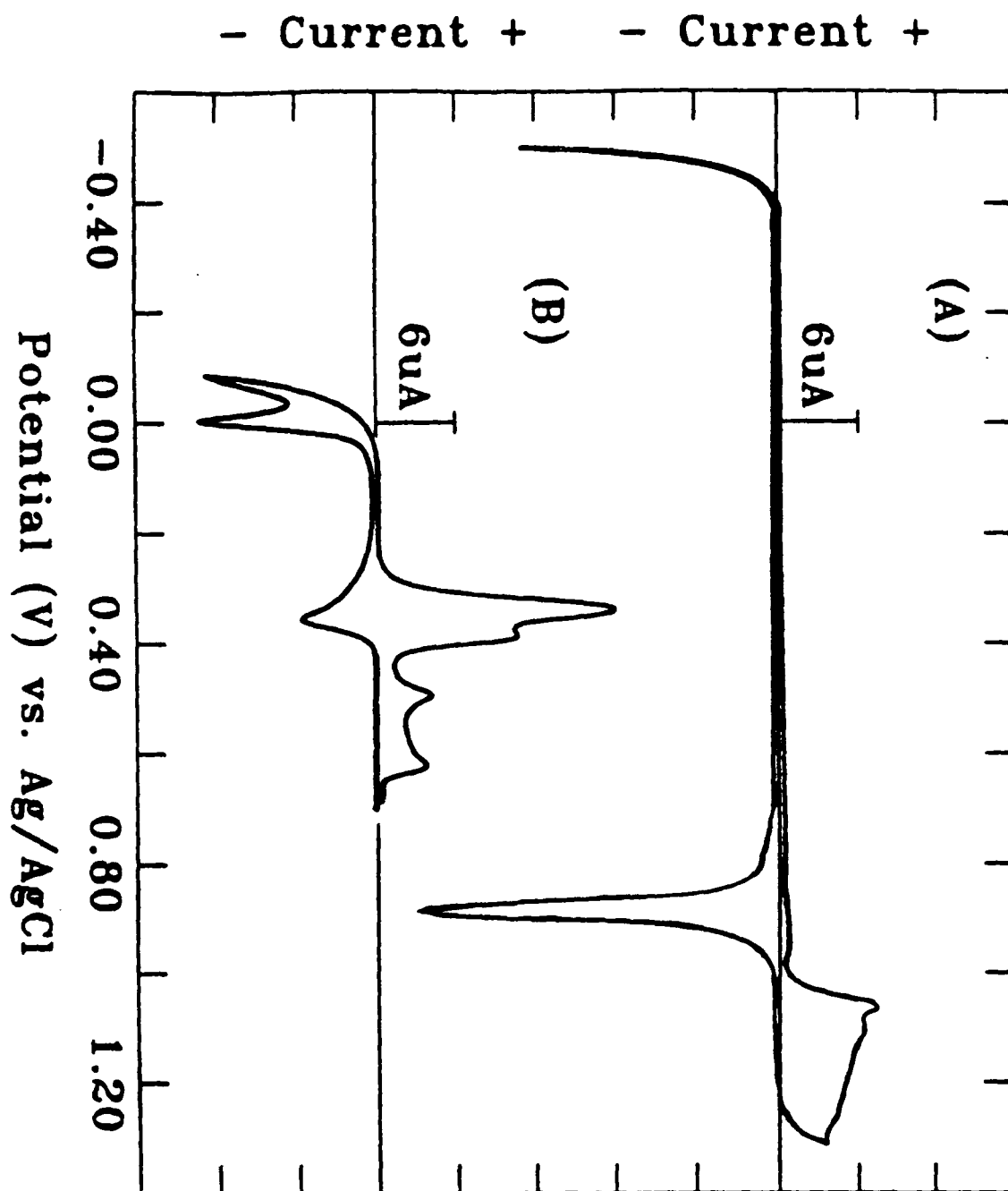


Figure 3 - Suggs, *et. al.*

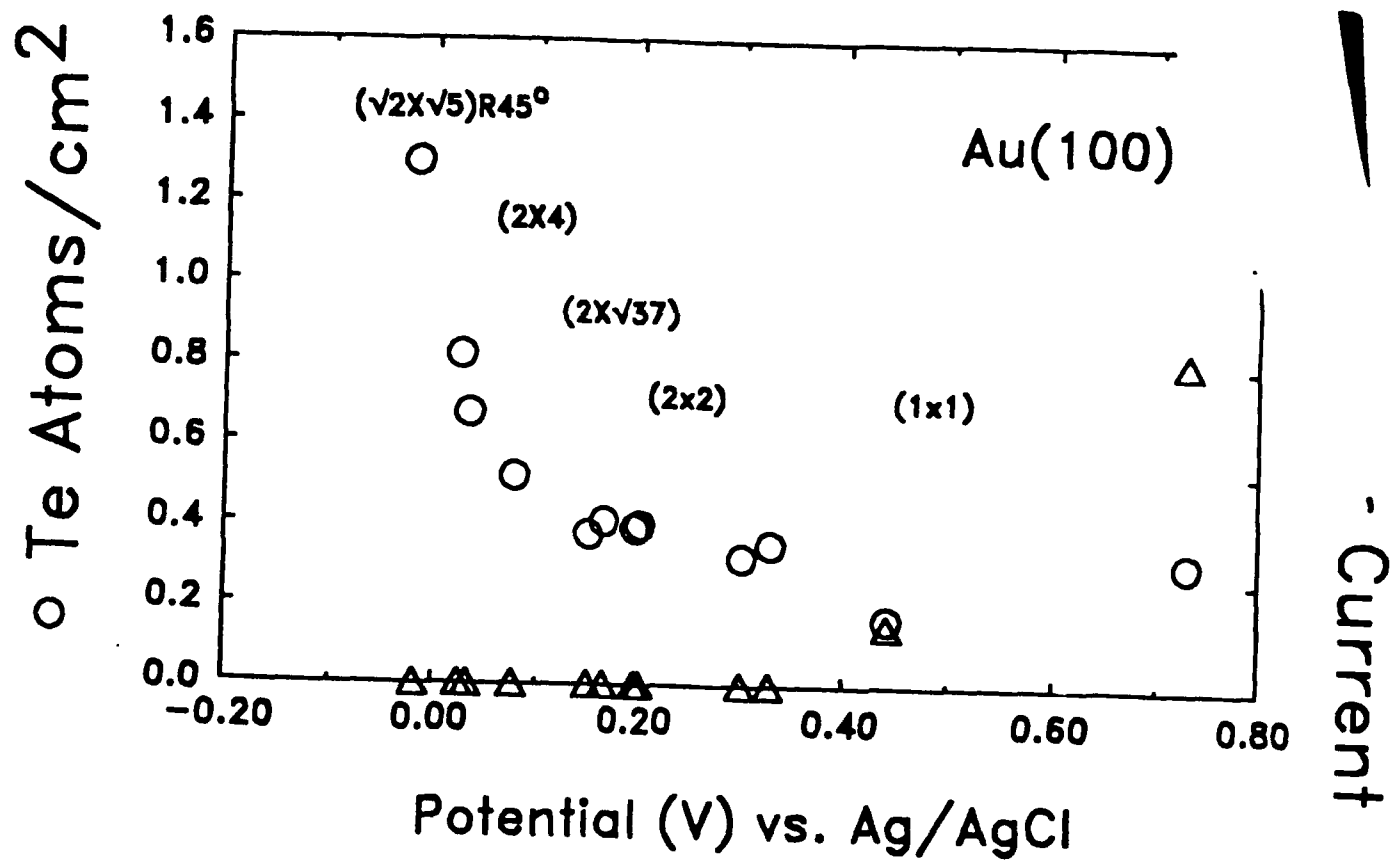


Figure 3 - Suggs, *et. al.*

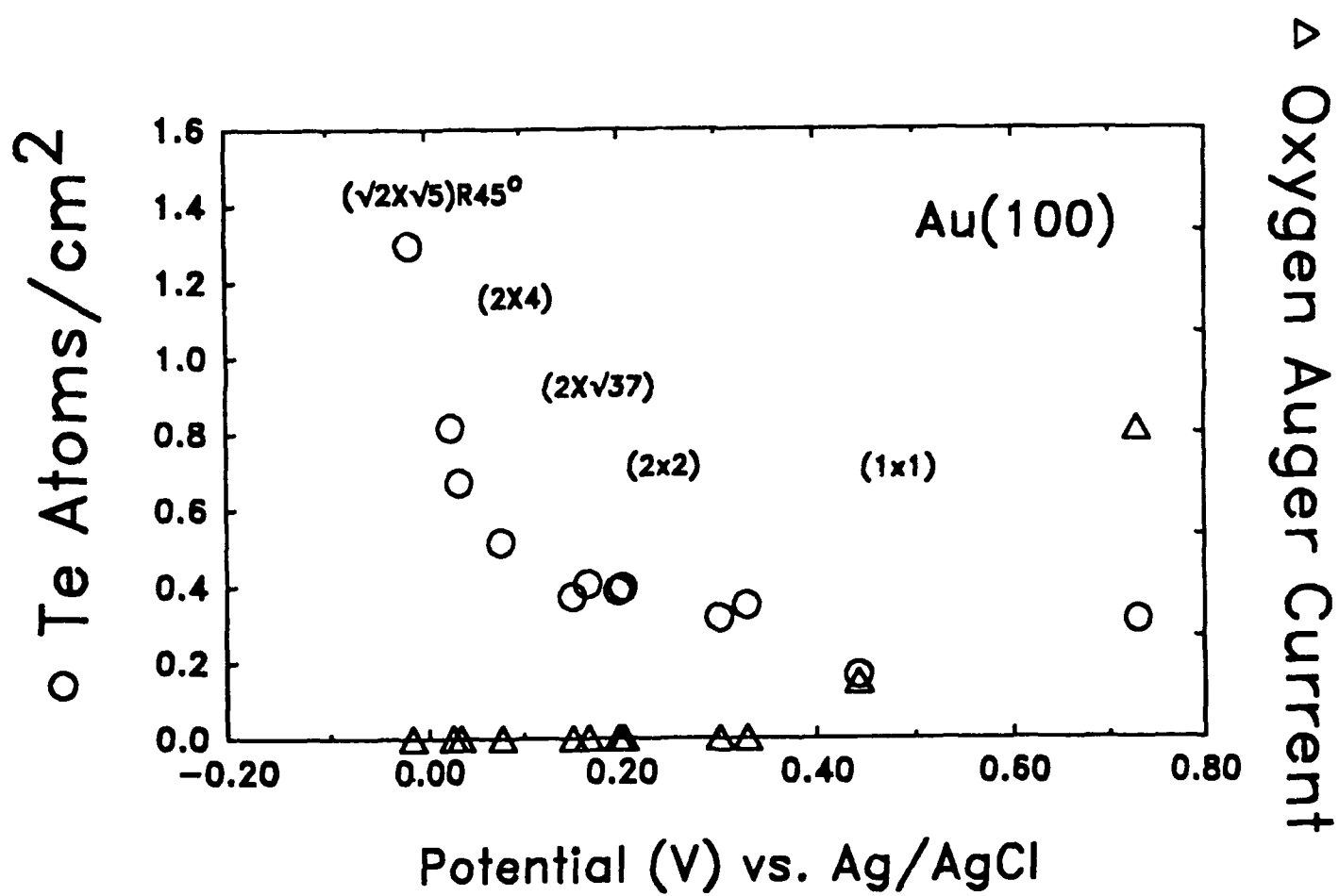
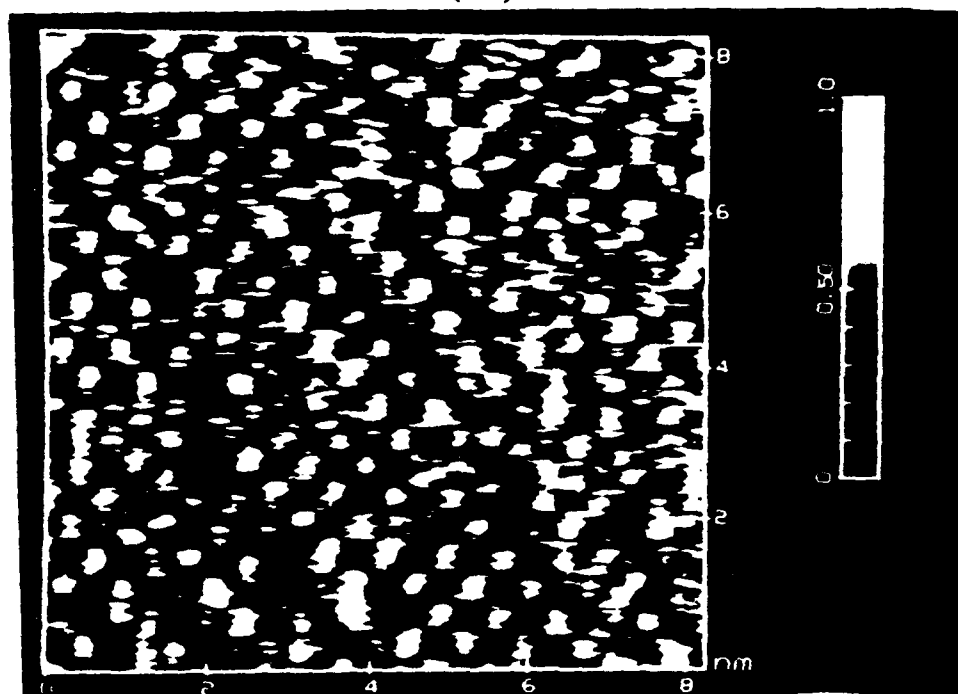


Figure 4 - Suggs, *et. al.*

(A)



(B)

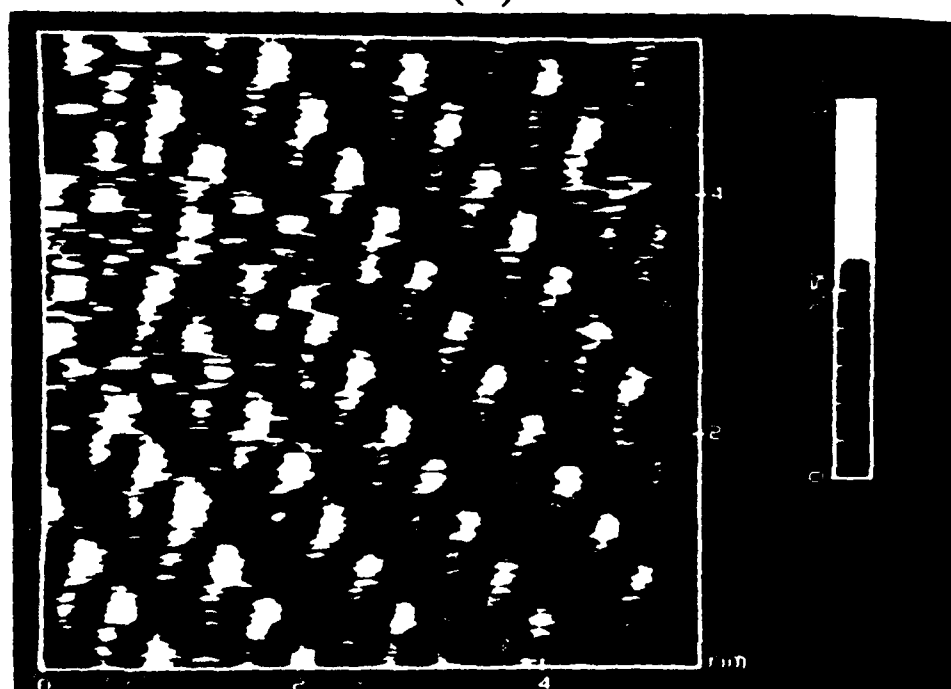
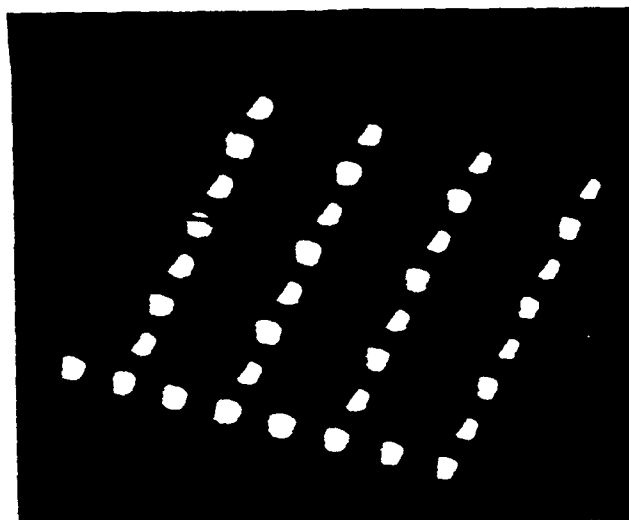


Figure 5 - Suggs, *et. al.*

(A)



(B)

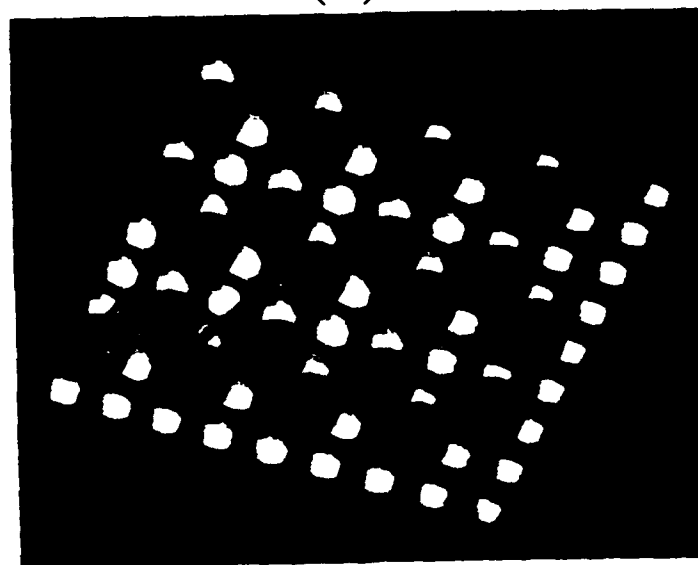


Figure 6 - Suggs, *et. al.*

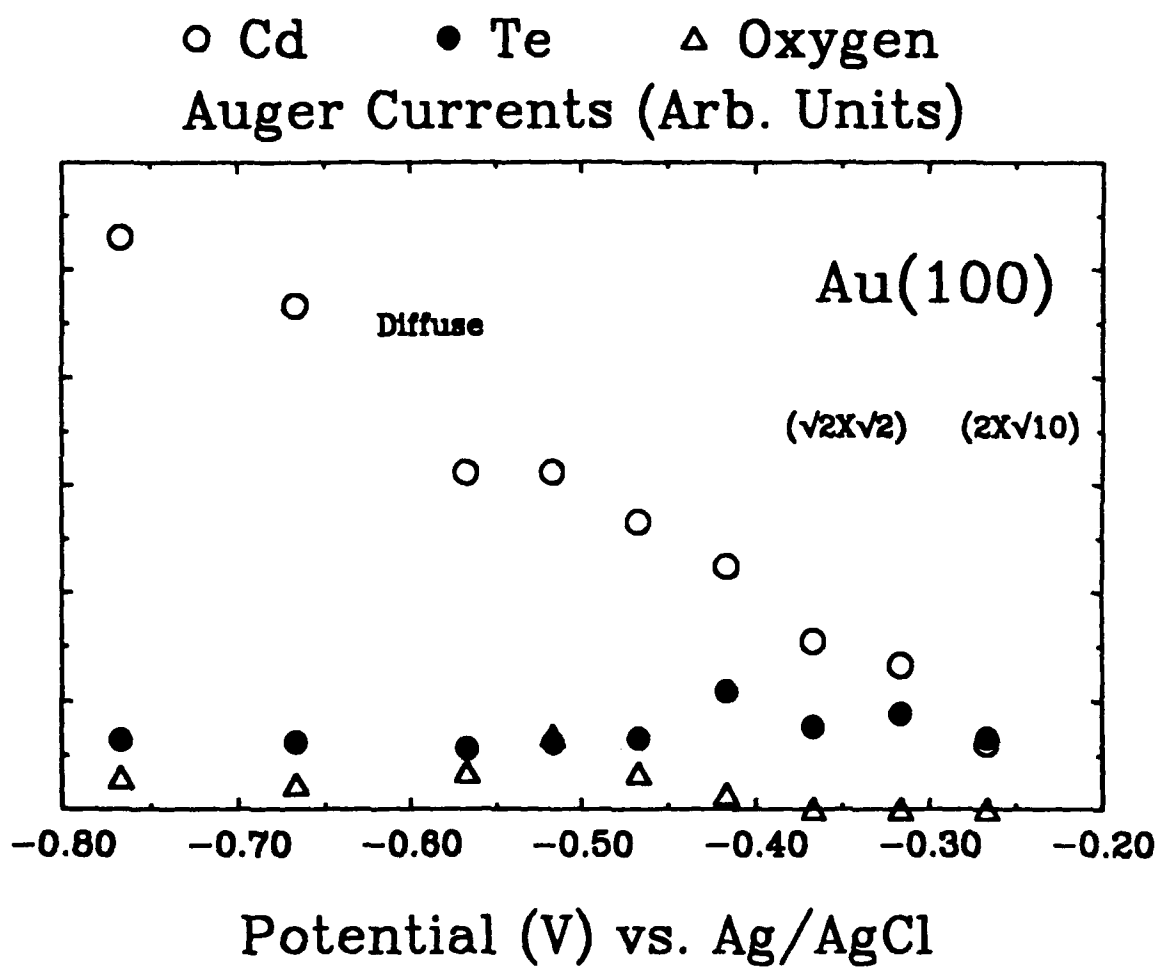
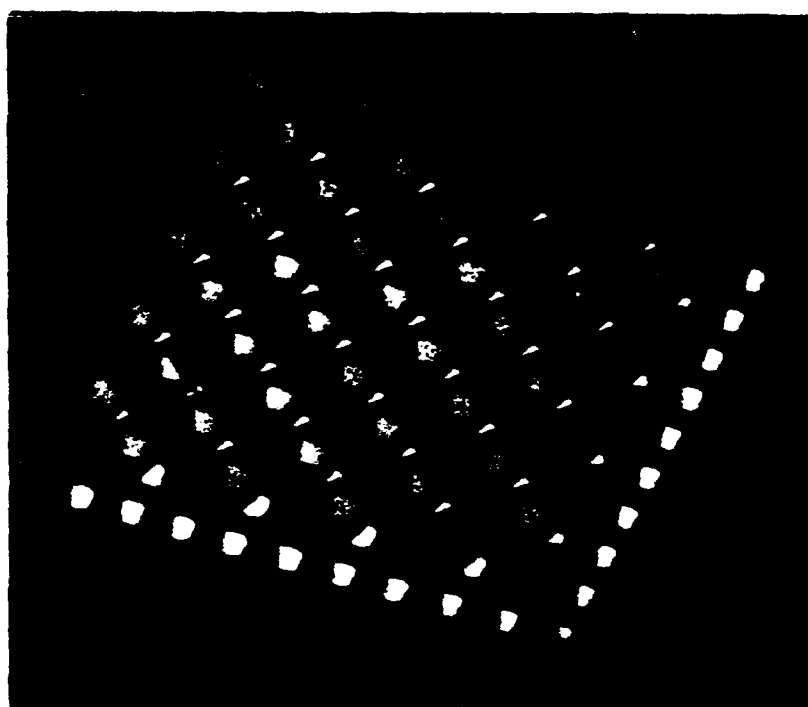


Figure 7 - Suggs, *et. al.*



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